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Title:	w17_mnccatalysis: Investigation of Structure and Reactivity Relationship in M-N-C Type Catalysts using Density Functional Tight Binding
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w17_mnccatalysis: Investigation of Structure and Reactivity Relationship in M-N-C Type Catalysts using Density Functional Tight Binding

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Scientific impact

1. Several electronic structure approaches were compared in their ability to model electron transfer reactions occurring on the solid-liquid interface. Specifically, we consider the oxygen reduction reaction as catalyzed at the interface of a N-doped graphene sheet and water. We ran the initial static self-consistent field relaxation of different systems (N-doped graphene, N-doped graphene and oxygen, oxygen and water, N-doped graphene with water, N-doped graphene with oxygen and water) to compare the convergence patterns of density functional theory (DFT), density functional tight binding (DFTB) with linear mixing and no Kernel, linear mixing with the rank-1 Kernel updates, and linear mixing with full Kernel updates. We found that converging the electronic problem with the Kernel and DFTB approximation was far more computationally efficient than DFT as evidenced by the time necessary to reach self-consistent field convergence for each system. The results further show that the rank-1 update during each self-consistent field iteration provides the best compromise for charge convergence and required computing time regardless of the system size (Figure 1). The computational resources were used to support mentoring of students during the Computational Physics Student 2018 Summer Workshop.

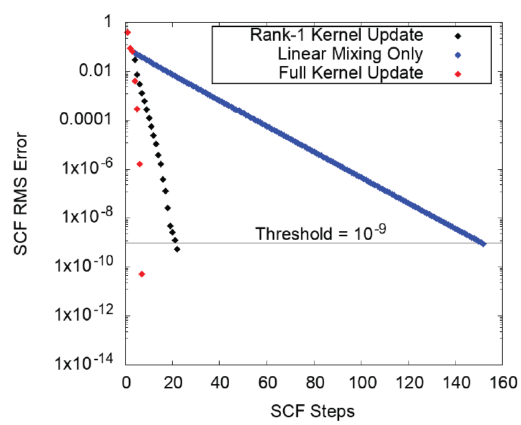

Figure 1. Logarithmic scaled self-consistent field error convergence for N-doped graphene with oxygen and water under the three Kernel schemes.

2. Density Functional Theory calculations were used to study the adsorption of nitrogen-free molecular probe based on 1-hydroxyethane 1,1- diphosphonic acid (HEDP) on different types of nitrogen and Fe−N_X moieties of M-N-C type oxygen reduction reaction catalyst. The computational results were used in combination with electrochemical and spectroscopic work to directly probe the competition between binding of oxygen and molecular probe to the surface of M-N-C catalyst and to identify the role of different types of nitrogen defects in the mechanism of oxygen reduction reaction. The results clearly identify the chemical structures that are responsible

for two parallel mechanisms of oxygen reduction reaction, via direct 4 electron reduction of oxygen to water, which occurs on iron coordinated to nitrogen $Fe{-}N_x$ sites, and via dual site 2×2 electron mechanism, where protonated and hydrogenated nitrogen catalyze the reduction of oxygen to hydrogen peroxide (Figure 2). Finally, it was found that HEDP is a unique inhibitor that has strong and partially irreversible adsorption to protonated and hydrogenated nitrogen, which increases the selectivity of the catalyst toward the 4-electron reduction of oxygen to water. The results are published in Y. Chen, I. Matanovic, E. Weiler, P. Atanassov, K. Artyushkova, Mechanism of Oxygen Reduction Reaction on Transition Metal-Nitrogen-Carbon Catalysts: Establishing the Role of Nitrogen- containing Active Sites, *ACS Appl. Energy Mater*, 1, 5948-5953 (2018).

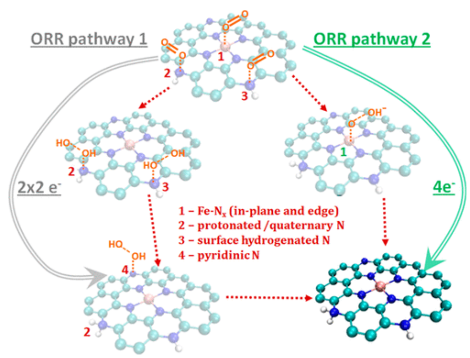

Figure 2. Calculations based on DFT were used to study the mechanism of oxygen reduction reaction on M-N-C catalysts by identifying actives sites that are blocked by the molecular probe used in the experiments.

3. Density functional theory calculations was used to study the adsorption of ionomer fragments based on benzene, biphenyl, and fluorene on the surface of Pt and Pt-alloy catalysts. We have shown for the first time that the hydrogen oxidation activity of Pt is inhibited by benzene adsorption. Using computations, we further demonstrated that bimetallic catalysts, such as PtMo/C, PtNi/C, and PtRu/C, can reduce the adsorption of benzene and thereby improve hydrogen oxidation activity. Namely, DFT results indicate that the adsorption of benzyl ammonium on the bimetallic PtRu is endergonic, which explains the significantly better hydrogen oxidation activity observed for the bimetallic catalysts. The results were further used to support a rational design of polyaromatic ionomers for anion exchange membrane fuel cells, which can minimize undesirable phenyl group interaction with hydrogen oxidation catalysts (Figure 3). The anion exchange membrane fuel cells using a newly designed aryl ether-free poly(fluorene) ionomer designed in MPA-11, LANL exhibited the peak power density of 1.46 W cm^{-2}, which is approaching that of Nafion-based proton exchange membrane fuel cells. The results were published in I. Matanovic, H. Taek Chung and Y. S. Kim, Benzene Adsorption: A Significant Inhibitor for the Hydrogen Oxidation Reaction in Alkaline Conditions, *J. Phys. Chem. Lett*. 8, 4918 (2017) and S. Maurya, S. Noh, I. Matanovic, E J. Park, C. Narvaez Villarrubia, J. Han, C. Bae, and Y. S. Kim, Rational design of polyaromatic ionomers for alkaline membrane fuel cells with >1 W cm^{-2} power density. *Energy Environ. Sci*, 11, 3283 (2018).

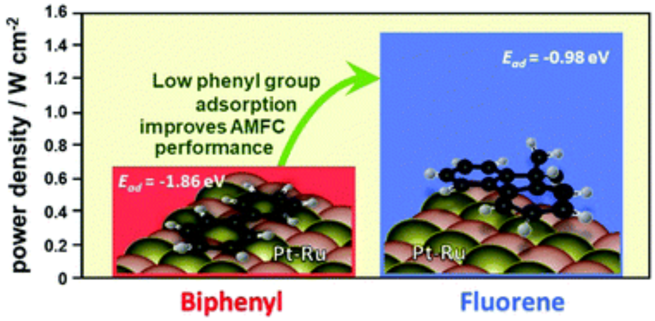

Figure 3. Calculations based on DFT were used to support rational design of polyaromatic ionomers in LANL that can minimize undesirable phenyl group interaction with hydrogen oxidation catalysts.

Publications (2nd year):

(1) I. Matanovic, H. Taek Chung and Y. S. Kim, Benzene Adsorption: A Significant Inhibitor for the Hydrogen Oxidation Reaction in Alkaline Conditions, *J. Phys. Chem. Lett*. 8, 4918 (2017).

(2) S. Maurya, S. Noh, I. Matanovic, E J. Park, C. Narvaez Villarrubia, J. Han, C. Bae, and Y. S. Kim, Rational design of polyaromatic ionomers for alkaline membrane fuel cells with >1 W cm^{-2} power density. *Energy Environ. Sci*, 11, 3283 (2018).

(3) Y. Chen, I. Matanovic, E. Weiler, P. Atanassov, K. Artyushkova, Mechanism of Oxygen Reduction Reaction on Transition Metal-Nitrogen-Carbon Catalysts: Establishing the Role of Nitrogen- containing Active Sites, *ACS Appl. Energy Mater*, 1, 5948-5953 (2018).

(4) K. G. Kleiner, A. Nair- Kanneganti, C. F. A. Negre, I. Matanovic, and Anders M. N. Niklasson, Modeling solid-liquid interface reactions with next generation extended Lagrangian quantum molecular dynamics, *manuscript in preparation*